

REMARKS

In order to allow full consideration of the foregoing amendments and the following arguments, Applicant is submitting concurrently herewith a request for continued examination.

In response to the provisional double patenting rejection, Applicant will provide a Terminal Disclaimer upon the identification of allowable subject matter.

Applicant submits that there are at least two fundamental reasons why the present claims are patentable over the cited Kukin, Kerley and Rolfe references. First, none of the references disclose use of organometallic manganese compounds that are mononuclear or comprise small clusters of manganese atoms to reduce the amount of carbon in ash resulting from the combustion of coal. The availability of manganese as a mononuclear compound or in small clusters, as defined in the application as referring to up to about 50 atoms of manganese, makes the manganese additive more dispersed or dispersable for positive catalytic effect. And second, there is a fundamental misunderstanding with respect to the definition of fly ash versus smoke and soot. These are physically different combustion products, and the effects on one are not related necessarily to the other.

In order to clarify the invention in specific terms, Applicant has included into the claims the definition that the manganese compound is mononuclear or comprises small clusters of manganese atoms. As defined in the description of the present application on page 4, compounds having "small clusters" of metal atoms can include those with about two to about 50 atoms of manganese. Manganese compounds that are mononuclear or that, in any event, have no more than about 50 atoms of manganese, allow for the metal atoms to be sufficiently dispersed or dispersable to be an effective catalyst for the combustion reaction. The size of the mononuclear compounds up to compounds that include small clusters of manganese atoms are extremely small. In this way, the manganese atoms are made available for the combustion reaction. Larger formations of manganese, for instance inorganic, crystalline forms, make the manganese atoms less available for reaction. As long as the manganese atoms are adequately dispersed in terms of single atoms or up to about 50 atom clusters, the manganese atoms are sufficient to provide a positive catalytic effect for the combustion reaction.

Turning now to the particulate by-products of the combustion of coal, Applicant believes that soot/smoke is a different type of combustion by-product than is fly ash. Manganese

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additives are known to catalyze carbon oxidation in smoke and soot. This catalization benefit is quite common in diesel fuel engines where the fuel is practically ashless and, therefore, can never effectively generate fly ash. The carbon oxidation benefit is also common in fuel oils burned in industrial and utility furnaces, because the ash level is so low that particulate by-products of combustion are mainly carbon with very little ash. In coals, however, since the amount of ash can range from 5% to 40% of the coal, it is necessary to differentiate between the soot/smoke component and the fly ash component of the particulate by-products of combustion.

Soot/smoke is generated from inefficient combustion of the volatile matter being expelled from the coal during the devolatilization stage of combustion and therefore has no ash in it. This is the component that colors flue gas black, and therefore, when it is contacted with a manganese-containing catalyst, it is oxidized and the color of the fly ash gradually lightens. On the other hand, carbon in ash and its behavior towards combustion catalysts is defined by the nature of dispersion of ash minerals in the coal carbon matrix. When the ash minerals are well dispersed, then the ash is said to be “excluded” and hence interferes less with the background carbon matrix during combustion. When the ash minerals are less dispersed and exist in islands in the coal carbon matrix, then the ash is said to be “included” and interferes with the combustion of carbon in and close to these ash islands. In most cases, both forms of ash dispersion exist in the same coal. For this reason, predicting whether or not a well known carbon oxidation catalyst, for instance, a manganese compound, will catalyze oxidation of carbon in fly ash from coal combustion is not a trivial assumption or prediction. For a more detailed discussion with respect to the science of ash versus soot/smoke, see the following article: Gupta, R.P., He, X., Ramaprabhu, R., Wall, T.F., Kajigaya, I., Miyamae, S., and Tsumita, Y.: “Excluded / Included Mineral Matter and its Size Distribution Relative Significance on Slagging and Fouling Characteristics”, in Applications of Advanced Technology to Ash-Related Problems in Boilers, pp. 245 – 264. Baxter, L., and DeSollar, R. Edits. Plenum Press. New York and London 1996. A copy of this article is attached hereto.

With the foregoing understandings as a basis, Applicant now turns to the four references specifically relied on by the Examiner in the Office Action in asserting that the claimed invention is obvious.

KUKIN ‘820

In the Office Action, the Examiner states that Kukin ‘820 does not disclose or explicitly

teach an organometallic compound. Instead, Kukin is said to teach a “manganese-containing substance”. As noted in the earlier discussion herein, it is believed that there is a significant physical distinction between inorganic substances generally that are made up of relatively large particles versus an organometallic manganese compound that includes small clusters of manganese atoms. Therefore, the failure of Kukin ‘820 to specify “organometallic” manganese is a significant failure of disclosure.

As also noted earlier herein, Applicant agrees with the Examiner in the Office Action that manganese is known to be a carbon-destroying catalyst in the context of smoke and soot. However, there is no discussion or disclosure of the use of manganese to affect the amount of carbon in fly ash. As detailed above, this is a significant distinction. This failure in disclosure is a significant failure that cannot be simply assumed away for purposes of obviousness.

KUKIN ‘503

The Kukin ‘503 reference corroborates the discussion above with respect to the difference between smoke and soot and fly ash. In Column 3 of Kukin ‘503, there is a specific discussion of how a manganese-containing preparation reduces smoke and soot. (Column 3, Lines 12-22). There is also a separate paragraph about how the specific manganese-containing preparation makes the combustion process less corrosive and forms less deposits in a furnace. (Column 3, Lines 23-43). Therefore, Kukin ‘503 explicitly draws a distinction between the effectiveness of manganese with respect to smoke/soot and fly ash. Kukin ‘503 recognizes fly ash separately from soot and smoke, and despite what might otherwise in hindsight be expected to be disclosed, Kukin ‘503 makes no mention of reduction of carbon in ash.

Additionally, Kukin ‘503 explicitly teaches away from the limitation that the manganese-containing additive is mononuclear or includes small clusters of manganese atoms. As set forth in Kukin ‘503, when the manganese is present in a particle size of less than .01 microns, the oxidized form of the manganese will form crystal growth patterns and agglomerate large size, manganese containing ash in the furnace. (Column 4, Lines 44-51). Therefore, Kukin ‘503 teaches that small particles of manganese (and Applicant notes that .01 microns is still far larger than that presently claimed) is harmful to a system. In other words, Kukin ‘503 explicitly teaches away from the use of a manganese-containing additive that includes small clusters of manganese atoms. (See also Column 5, Lines 30-36). In summary, Kukin ‘503 explicitly teaches away from

the claimed invention both from the perspective of small clusters of manganese atoms and from the perspective of the effect of manganese on fly ash being materially different from the effect in oxidizing soot/smoke.

Finally, for completeness, the Examiner refers to Table 1 of Kukin '503. Instead, Applicant would refer the Examiner to Tables 1-4 in which the use of an organometallic manganese compound is shown to be unfavorable with respect to the negative ash properties of agglomerating ash on the inside of furnaces. In each example, the organometallic additive does NOT deliver the benefits sought for and described in the patent. Therefore, the specific examples of Kukin corroborate the fundamental argument of Applicant that it would not be obvious to assume that a manganese-containing compound would reduce carbon in fly ash.

KERLEY

Applicant has carefully studied the Kerley reference and found no disclosure of the effect of carbon in fly ash when a manganese-containing compound is combusted with coal. Instead, there is only the disclosure and discussion with respect to the reduction of smoke and soot. As detailed earlier, there is a significant difference between the combustion particulate products of smoke and soot and fly ash. This difference is confirmed in at least the cited Kukin '503 reference which notes the difference between soot and smoke and fly ash. Without any disclosure of the effect in the combustion of fly ash, it is not obvious that Kerley teaches or suggests the use of a manganese compound to reduce carbon in ash.

ROLFE

Applicant believes that Rolfe is not a reasonable reference that teaches the reduction of carbon in fly ash from the combustion of coal. Rolfe teaches that his manganese complex can be sprayed on solid fuels prior to combustion. Further, Rolfe teaches that his invention may reduce smoke emission. However, there is no specific disclosure that manganese reduces the amount of carbon in ash. The Examiner's attention is specifically drawn to Column 6, Lines 27-56 of the Rolfe reference. In that paragraph, it is described by Rolfe that the amount of carbon deposits is reduced or disappears altogether from a combustion chamber. However, it is also noted in Rolfe that the bag filters and electrostatic precipitators further down in the combustion process contain the deposits that are moved out of the combustion chambers where the carbon deposits would

otherwise be found. In other words, Rolfe does not stand for any proposition that there is a reduction of carbon in ash. Instead, Rolfe merely demonstrates that the fly ash is moved from a deposit inside the combustion equipment to a deposit in a bag filter or electrostatic precipitator.

CONCLUSION

For one or more of the foregoing reasons, Applicant submits that the application is in condition for allowance. The limitation of the present invention to manganese compounds that contain mononuclear or small clusters of manganese atoms is a significant clarification of the invention. Further, the difference between carbon in ash and soot/smoke is a significant one. Applicant respectfully submits that the references cited by the Examiner do not reasonably disclose nor render obvious the claimed invention. The rejections are traversed and Applicant respectfully requests that they be withdrawn.

FEES

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Respectfully submitted,

A handwritten signature in black ink, appearing to read "Dennis H. Rainear", with a stylized flourish at the end.

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EXCLUDED / INCLUDED MINERAL MATTER AND ITS SIZE DISTRIBUTION RELATIVE SIGNIFICANCE ON SLAGGING AND FOULING CHARACTERISTICS

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ABSTRACT

The effect of the nature of mineral matter (extraneous or inherent) on combustion generated ash is investigated by means of thermodynamic calculations and combustion experiments in a drop-tube furnace. Five coals, including one high in silica, one high in calcium and magnesium and one high in iron, were analysed for mineral matter size distribution using the CCSEM technique. The particle size distribution of mineral matter is found to be bi-modal in nature. The coal samples are found to have included mineral matter smaller than 20 μm whereas the excluded mineral is mostly larger than 40 μm in size.

The nature of mineral matter determines its reactions during combustion; the excluded mineral matter is in equilibrium with the bulk flue gases at the gas temperatures whereas the included minerals are in equilibrium with char at the burning char particle temperature. It is predicted from the thermodynamic calculations that almost all the evaporation is either from the included mineral matter or from the atomically dispersed minerals in coal. This is due to the high temperature and reducing atmosphere inside the char particle. The release of the evaporated species is controlled by diffusion through the burning char particle and may be, therefore, estimated theoretically.

The theoretical predictions of the ash character so derived are compared with the experimental data obtained by firing the coals in 10%, 23% and 50% oxygen in a drop tube furnace. The amount of mineral matter that is vaporised may be related to fouling, whereas, the melt phase present on the surface of large particles may be related to slagging. The mineral matter distribution is, therefore, related its effect on these two factors.

1. INTRODUCTION

In previous work (Gupta and Wall, 1993), Newlands, Daido and Miike coals were investigated for their depositional characteristics. The present study investigates the effect of the nature and the size distribution of mineral matter in these coals. It includes two new coals containing high levels of silicon, calcium and magnesium, namely Ulan coal (from Australia), and Medicine Bow coal (from USA). The standard ash analyses are presented in Table 1. The ash from Ulan coal is rich in silica (85%), the ashes from Daido and Miike coals are high in iron (9-10%), and the ashes from Miike and Medicine Bow are high in calcium and magnesium (25-40%).

The mineral matter within the coal matrix is called included minerals, whereas the discrete particles of minerals not associated with carbonaceous matter are called excluded minerals. In pulverised fuel, the amount of excluded mineral increases with increased grinding. The physical (eg size and density) and chemical (eg composition of mineral phases) characteristics of mineral matter relate to several factors associated with ash deposition: the evaporation of mineral species, the size distribution of ash, and the composition of the sticky exterior layer of the coarse ash particles formed during combustion. These factors influence the ash transportation to walls and its stickiness.

The coal samples used in the ash formation experiments were sieved to a narrow size fraction of 63-90µm. The experiments were conducted in a drop-tube furnace under different environments (1200°C, 1350°C and 1500°C, and at oxygen concentrations of 10%, 23% and 50% by weight). The ash was separated into fines (< 2µm) which are rich in fumes and coarse ash. The chemical analysis of coarse ash was determined by the XRF technique. The acid soluble oxides in fine ash and coarse ash were determined by the Atomic Absorption technique to obtain the composition and amount of the fines and fumes.

The same size fraction samples were examined for mineral matter size distribution by the Computer Controlled Scanning Electron Microscopic (CCSEM) technique at the Energy and Environmental Research Center (EERC) at University of North Dakota. The CCSEM data include the particle size distribution of both the included and the excluded mineral grains, along with the chemical composition of each mineral grain. Figure 1 shows the heterogeneous composition of mineral grains (detected by the CCSEM only) in four of the coals. Organically associated inorganics are expected to be distributed uniformly within the char matrix.

The mineral matter details from the CCSEM analysis are used to provide the effective ash composition that is in equilibrium with the surrounding gases. The included minerals are in equilibrium with char (expressed as carbon) at the temperature of the char particle for estimating the amount of the minerals evaporated. The equilibrium of the excluded mineral with flue gases at the gas temperatures is used to estimate the characteristics of sticky molten phase on coarse particles. Thermodynamic equilibrium calculations for the excluded and included minerals are thus performed separately.

The experimental results from the ash formation experiments are compared with the theoretical estimates for the amount of fumes generated and the amount of molten phase and its composition.

1.1 Literature Review

Couch (1994) has given an extensive survey of the current status and research related to ash deposition. The following points are the main conclusions from the literature review:

- Mineral matter in coal and the combustion environment are the two key factors that influence the ash formation process.
- The fraction of mineral matter in coal, its form and particle size distribution is also related to the ash formation process. Advanced techniques such as CCSEM (Skorupska and Carpenter, 1993) and Quantitative Evaluation of Materials by Scanning Electron Microscope QEM*SEM (Gottlieb et al., 1992) are able to provide detailed information on the mineral matter necessary for development of new indices for fouling and slagging.
- The combustion environment influences the temperature of the burning particle and thus enhances the vaporisation of included minerals within the char matrix and thereby influences the amount of fume formation.
- The particle size distribution of fly ash is known to influence the rate of its transportation. Fine particles are transported by thermophoresis, whereas larger particles are mostly transported by inertial impaction. Models can predict the ash PSD from the mineral matter distribution (Beer et al, 1991; and Wilmski et al, 1991).

1.2 Mineral Matter in Coal

The three aspects of mineral matter influencing the ash formation are: nature of mineral matter - (included or excluded), particle size distribution and form of mineral matter.

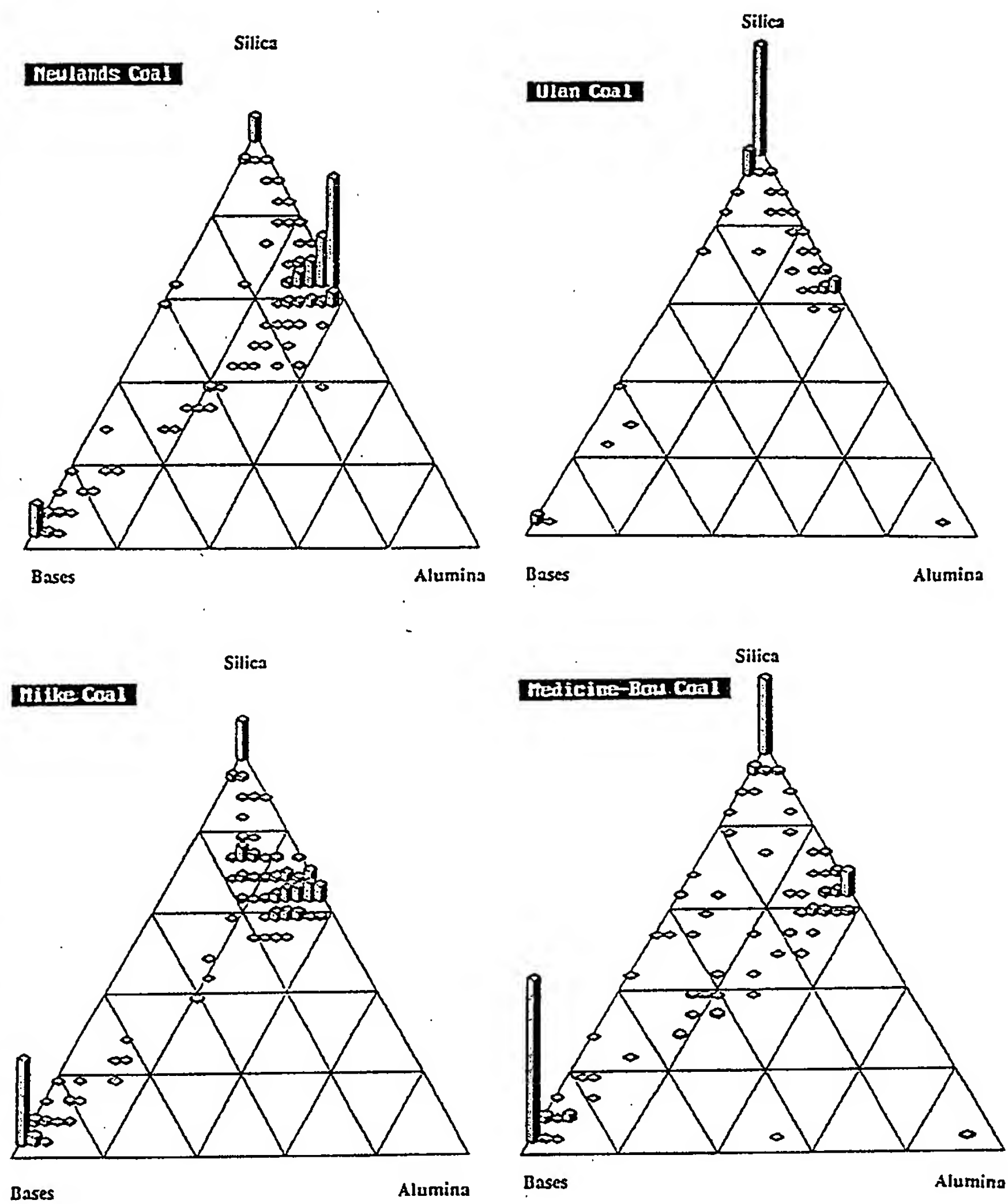


Figure 1. Mineral matter distribution for four coals from CCSEM analysis

Nature of Mineral Matter: The extraneous mineral matter, the mineral matter within the coal matrix and the organically associated inorganics produce ashes of varying character. The association of included mineral matter with char also increases the evaporation of mineral species significantly (Boni et al. 1990). The mineral matter within the coal matrix reacts and evaporates under more severe conditions (a reducing atmosphere and high temperature) as compared to the extraneous mineral matter. The inherent minerals are physically close and therefore can react easily. In addition, a part of these mineral inclusions may melt and coalesce to form dense ash particles.

The mineral particle size distribution (PSD): A large mineral grain is less reactive than a small mineral grain, as a large mineral grain may participate partially in ash reactions. The evaporation of silica increased from 5% to 40% in 50% oxygen and 1650K when the quartz grain size decreased from 10 μ m to 2 μ m (Boni et al., 1990). Previous thermodynamic calculations (Gupta and Wall, 1993) also predicted a significant effect of size distribution of mineral matter on the evaporation of alkalis shown in Figure 2. In this figure $AC=0.1$ for silica and alumina implies that only 10% of these oxides are available for thermodynamic equilibrium.

Mineral Matter Form: The vaporisation of silica and calcium is strongly influenced by their mode of occurrence. Their presence as large discrete extraneous minerals may not enhance slagging. Silica may be present in the form of quartz, illite and kaolinite. However, silica in the form of quartz is relatively least reactive but in the form of illite it will coalesce with other minerals rapidly. Similarly, calcium and magnesium in illite react rapidly, but if it occurs in the form of carbonates (eg calcite and ankerite) large mineral grains fragment increasing the viscosity of the molten phase (Zygarlicke et al. 1991).

This suggests that for high silica and calcium coals, it is not the amount of the species that is critical, but it is the form of that mineral, the fraction present as included minerals and its grain size that would influence slagging or fouling tendencies. The excluded calcium, for example, would contribute to fouling, whereas the included calcium (in presence of silica) would form low melting point complexes enhancing slagging tendencies. Iron present in the form of pyrites is slowly oxidised with some fragmentation in presence of oxygen, whereas, iron in the form of ankerite or siderite is prone to severe fragmentation to 0.1-1.0 μ m size particles (Raask, 1985). However, sodium and potassium would vaporise irrespective of how they occur.

1.3 Combustion Environment

The combustion environment influences ash formation in two ways: the temperature of the char particle during combustion and the particle size distribution of ash. Gas temperature and the amount of excess air determine the evaporation of mineral species. The vapour pressure of the mineral species increases exponentially with temperature. Thermodynamic calculations (Gupta and Wall, 1993) predicted sharp increases in fume formation with increase in gas temperature. The vaporisation was also enhanced by a reducing atmosphere (Figure 2). The particle temperature is strongly influenced by the oxygen concentration. A higher particle temperature subsequently increases the evaporation of the included mineral species. Erickson et al. (1992) found the mass median diameter of the ash samples formed from synthetic char at 900°C and 1500°C to be 15 μ m and 40 μ m, respectively.

1.4 New Characterisation Techniques

Kalmanovitch (1991) has suggested a technique to present detailed information on mineral matter and ash in form of a distribution curve. The curves show the percent of ash that will be present as a molten phase at a given temperature.

Zygarlicke et al. (1991) have also proposed some performance indices based on CCSEM analysis. The criteria used in developing the indices is based on the following factors: clay content facilitating formation of low melting point compounds (LMPC), fine and included quartz content which is more reactive, calcite content which may increase the viscosity thereby decreasing the deposit strength, and organically bound sodium and calcium content which result in the formation of LMPC.

Gupta and Wall (1993) have suggested the amount of sodium and iron present in gas phase per unit of coal consumed as indicators for fouling and slagging, respectively. These indices account for mineral

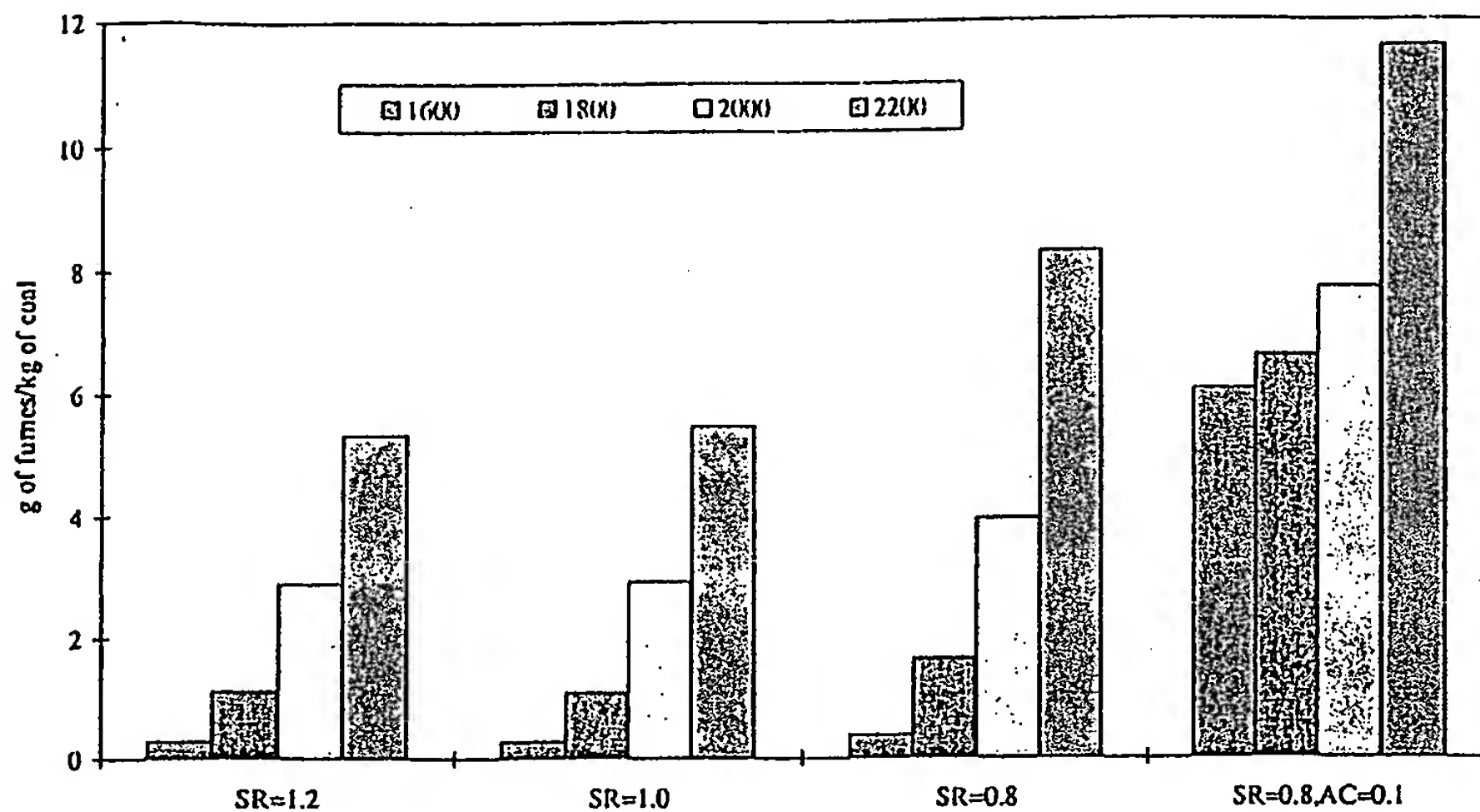


Figure 2. Effect of operating conditions (four combustion temperatures and several stoichiometric ratios) and mineral matter size (AC for silica and alumina being 0.1) on evaporation of alkalis.

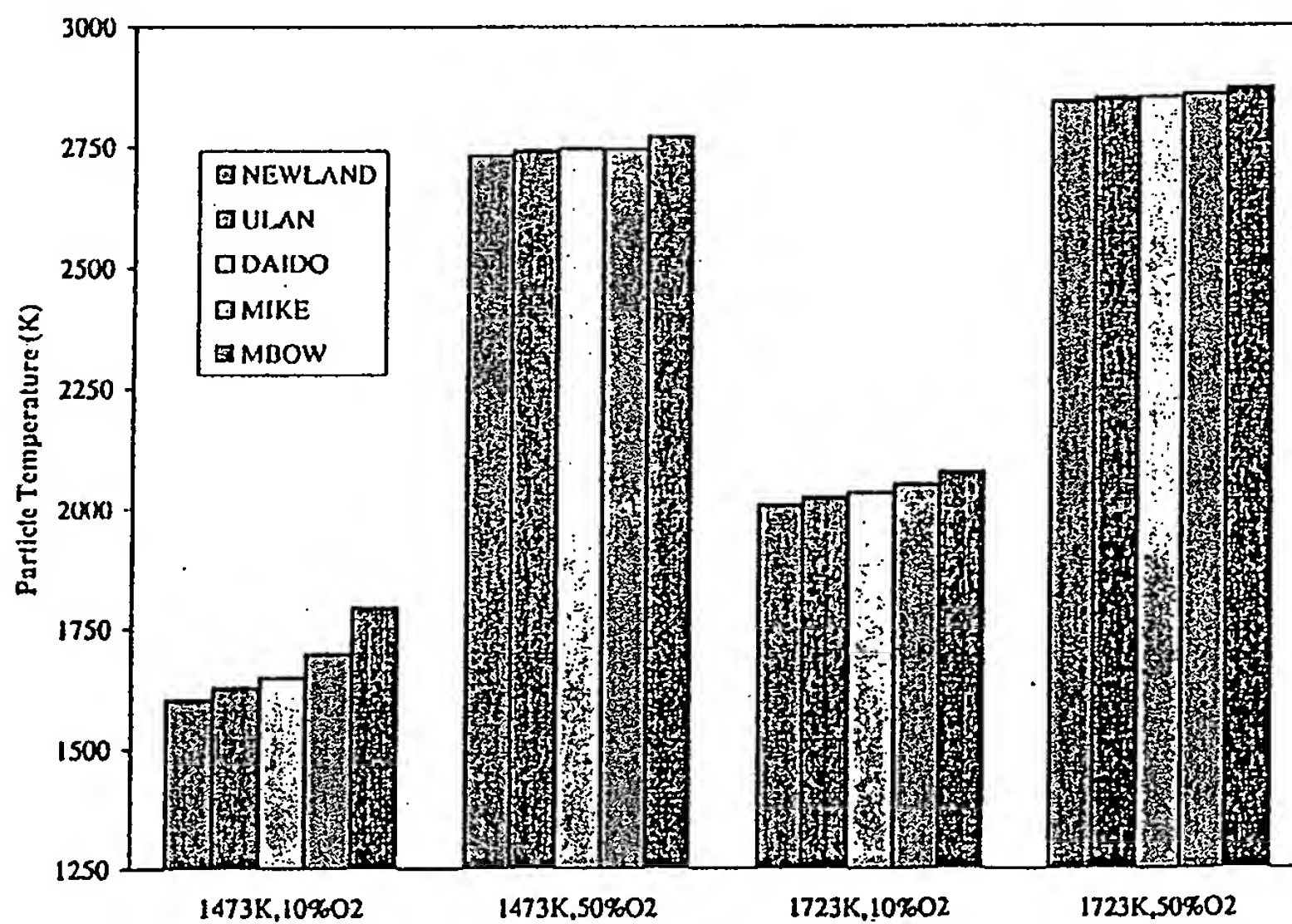


Figure 3. Predicted temperatures of burning char particles of 80µm in different combustion environments for five coals.

matter distribution and the operating conditions of the boiler, which are further investigated and modified in this project.

Stickiness has been considered a function of viscosity of particles at some effective particle temperature so that the most common stickiness models relate to the viscosity of particles (Benson et al., 1993). The stickiness of the ash particles is quantified by the ratio of a critical or reference viscosity to the viscosity of particles at particle temperature. The main limitation in these models is the uncertainty in the value of critical viscosity. The viscosity of the fly ash can be obtained from ash composition by using the correlation of Urbain et al. (1981). The model was developed to estimate the alumio-silicate based ceramics. There have been some modifications for ashes with high iron content.

1.5 High silica and high calcium coals

A study at MIT (Graham, 1991), focussed on the reactions of silica and calcium; the analysis showed the final products formed from calcium consisting of CaO, CaSiO₃ and Ca-Si glasses. Calcium and magnesium are present in coal in the form of carbonate clays ie calcite, dolomite and ankerite. In another study on the behaviour of calcium in low rank coal, Beulah lignite, (Shah et al., 1991, and Srinivasachar et al., 1991), the ash samples prepared in a laboratory combustor were size graded by Anderson impactor. Most of the calcium (organically associated) reacts with aluminosilicate to form calcium aluminosilicate of varying composition. Calcium rich particles (mostly unreacted CaO particles from calcination of calcite) were found mainly in the first impactor (>9µm). In the samples from other impactors (<9µm) calcium rich particles decreased. Zygarlicke et al. (1991) also indicated that organically bound calcium quickly reacts with aluminosilicate and quartz within the coal matrix forming lower melting point phases eg CaSiO₃. However, large discrete grains of calcite may act as diluent and may increase the viscosity of liquid phases.

In all the five coals investigated in the present study, calcium is mostly in the form of calcite. The above mentioned research indicates that the assessment of high silica or high calcium coal requires detailed knowledge on the form of the minerals, the size distribution of these minerals in the coal matrix and their association with each other. The CCSEM analysis is a critical factor in evaluating their ash deposition characteristics.

2. TEMPERATURE OF BURNING CHAR PARTICLE

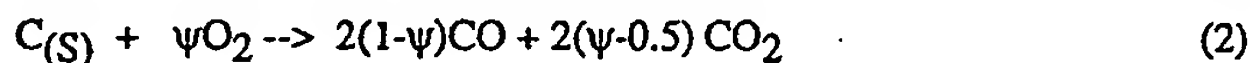
The mineral matter associated with carbonaceous matter in pulverised coal (ie included minerals) attains the temperature of the burning particles. It has been shown experimentally that the temperature of a burning particle can be 400°C higher than that of the surrounding flue gases depending on the particle size, oxygen concentration and the combustion kinetics (Timothy et al. 1985). This requires a good knowledge of the particle temperature during combustion. This section deals with the estimation of such temperatures for burning char particles. The excluded minerals, fed to the furnace as discrete particles, are essentially in thermal equilibrium with furnace gases.

2.1 Model for burning char particle

The particle temperature may be determined by equating the heat generated from char combustion to the heat losses due to convection and radiation. The rate of heat generation, Q_{gen} , by a particle is given by the following equation;

$$Q_{gen} = m \Delta H_c \quad (1)$$

where m - rate of combustion (gram of char consumed per second)
 ΔH_c - heat of combustion per gram of char consumed by the following reaction:



where ψ is the number of moles of oxygen consumed per mole of carbon and determines the ratio of the

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combustion products CO and CO₂. Values of ψ of 0.5 and 1.0 correspond to the complete combustion to CO and CO₂, respectively. Tognotti et al. (1990) obtained experimentally the value of ψ as 0.52 and 0.59 at 20% and 100% oxygen levels, respectively, for a 130 μ m particle. Boni et al. (1990) referred to a study where it was found that ΔT_p is proportional to r_p^2 and $(\psi-0.5)^{0.7}$. The value of ψ is, therefore, obtained by the following empirical equation;

$$\psi = 0.5 + [0.502 + 0.0877X_{O_2}](D_p(\mu\text{m})/130)^{1/0.7} \quad (3)$$

The rate of char combustion is usually expressed by the following expression.

$$m = k_s P_s^n \quad (4)$$

$$k_s = A \exp(-E/RT_p) \quad (5)$$

where m is the combustion rate kg-carbon/(sec-m² of external surface area) and n is the global reaction order. The global combustion rate, k_s , includes the effects of pore diffusion, internal surface area and intrinsic surface reactivity, and is given by equation (5).

Hurt and Mitchell (1992) developed a generalised correlation that allows the prediction of char combustion rates for a range of coals as a function of carbon content. These correlations, assuming the reaction order of half with respect to oxygen, reproduced the combustion rates within 30% at gas temperatures of 1250°C to 1750°C. In the absence of kinetic data for the five coals investigated in the present study, the above correlations are used to predict the temperature of the burning char particle.

The rate of heat loss from the particle includes the conduction and radiation losses to the surrounding environment.

$$Q_{\text{loss}} = 4\pi r_p k_{\text{eff}} (T_p - T_g) + \sigma (4\pi r_p^2) \epsilon_p (T_p^4 - T_g^4) \quad (6)$$

ϵ_p is the emissivity of the particle. The value of the particle emissivity is assumed to be unity. The effective thermal conductivity, k_{eff} , of the gases in the boundary layer around the particle is evaluated at a mean temperature of T_p and T_g . The dissociation of oxygen is taken into account as it influences the thermal conductivity significantly at high temperatures.

Timothy et al. (1982) measured the particle temperatures of Montana lignite and Illinois #6 coal at 1700 °K in oxygen concentration varying from 10-100%. The two coals have 74% and 70% carbon content on dry ash free basis; respectively. The present model was used to determine the temperatures of 130 μ m size char particles of Montana lignite and Illinois #6 coals in different oxygen environments during combustion. The predictions for the Montana lignite are slightly (40-60°C) lower than those for Illinois #6 due to its lower reactivity, whereas the measured temperatures for the Montana coals are a few hundred degrees lower than those for the Illinois #6. The results compare very well with those for Illinois #6 coal.

2.2 Particle Temperature of Test Coals

Figure 3 compares the predicted temperature of 80 μ m for the coals in different combustion environments. The particle temperatures of the five coals vary in the order of reactivity ie Newlands, Ulan, Daido Muike and Medicine Bow; Newlands being the least reactive and Medicine-Bow being the most reactive coal. The particle temperature is clearly influenced to a greater extent by the oxygen concentration than by the surrounding gas temperature.

Low oxygen concentration (10%): In an environment of 10% oxygen and gas temperatures of 1200°C gas temperatures, the particle temperature for Newlands is 125°C, and for Medicine-Bow 320°C higher than the surrounding gas temperature. The difference in coal type is most significant in a kinetics controlled regime at 1200°C; the particle temperature of Medicine-Bow is 195°C higher than that of Newlands coal. At a gas temperature of 1450°C, the particle temperatures of different coals are estimated to differ only by 70°C, (the particle temperature being 2010°C for Newlands and 2080°C for Medicine-Bow coal).

Oxygen Concentration (50%): The combustion regime changes from kinetic control to diffusion control due to an increase in oxygen concentration or gas temperature. The temperature of a burning particle can be as high as 2500°C in the 50% oxygen environment and is not influenced by the gas temperature. The difference between the particle temperatures for the five coals diminishes to 40°C at 1200°C gas temperature and to 30°C at 1450°C gas temperature.

In PF boilers, the oxygen concentration is usually less than 10% during the char combustion. Results from the sensitivity analysis indicated that a finer grind of coal particles would then lead to lower burning particle temperatures resulting in less evaporation of mineral matter. The fine particles (< 10µm) of high rank coals may burn within 50°C of the gas temperatures in a low oxygen (<5%) atmosphere. A finer grind would also result in a smaller proportion of included minerals. The oxygen concentration does not influence the behaviour of the excluded minerals. A further conclusion is: the thermodynamic calculations may be performed at the same particle temperature irrespective of the coal rank while analysing the drop-tube furnace experiments conducted at high temperature and high oxygen concentration.

3. THERMODYNAMIC CALCULATIONS

The theoretical estimates for the formation of fines and fumes, and for the amount and composition of the molten phases on sticky particles were obtained from thermodynamic equilibrium calculations using a chemical equilibrium program CHEMIX, developed by CSIRO Australia (Gupta and Wall, 1993). The program computes the equilibrium compositions in different phases by minimising Gibbs free energy. The inputs to the CHEMIX program are the products resulting from the combustion of coal including the ash components.

The theoretical estimates of ash vaporisation and the molten phase are modified here by means of three considerations;

- The use of an availability coefficient
- Temperature estimates of the burning char particle
- Presence of char for the included minerals

3.1 Availability Coefficient

The effect of mineral matter grain size on its evaporation has already been demonstrated experimentally (Boni et al., 1990). Wibberley and Wall (1982) estimated the thickness of a reacted sticky layer on silica particles to be 0.1-0.3µm, when silica was fed into the drop-tube furnace with sodium salts. This implied that the core of the particle does not react. The mass fraction of the reacted layer to the total mass of the particle is referred to here as the availability coefficient (AC).

The equilibrium calculations assume the activity of all the ash components as unity, as if all the components are freely available for reaction. The estimates for alkali vaporisation were under-predicted by this approach when compared with results from the drop-tube furnace experiments. With an arbitrary value of availability coefficient of 0.1 for silica and alumina (only 10% of silica and alumina is reactive), these estimates were found to improve (Gupta and Wall, 1993). The availability coefficient (AC), therefore, may also be defined as the fraction of the minerals actively participating in the establishment of the thermodynamic equilibrium. A lower availability of silica and alumina for example increased the vaporisation of alkali species and reduced the evaporation of silica and alumina.

The estimates for evaporation of mineral matter, the amount and composition of the molten phase are made for the five coals (Newlands, Daido, Miike, Ulan and Medicine-Bow). The mineral matter grains in the coal vary in size, and the PSD of the mineral grains from a CCSEM analysis was used to determine the AC of individual species. The CCSEM determines the size distribution of both included and excluded mineral matter.

The CCSEM data are processed into 50 equal size fractions from 0-100 µm. The particle size distribution

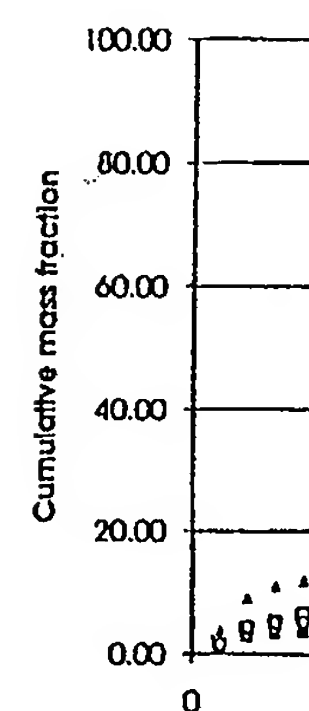
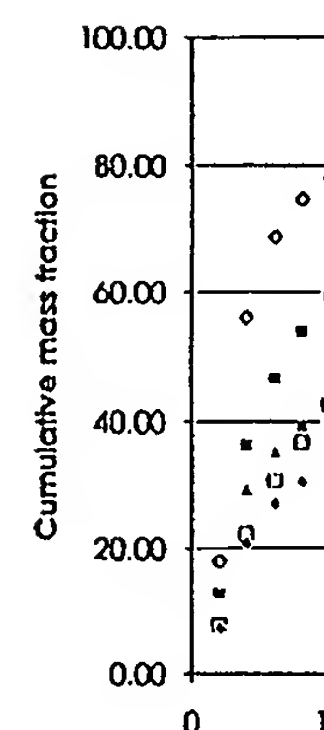
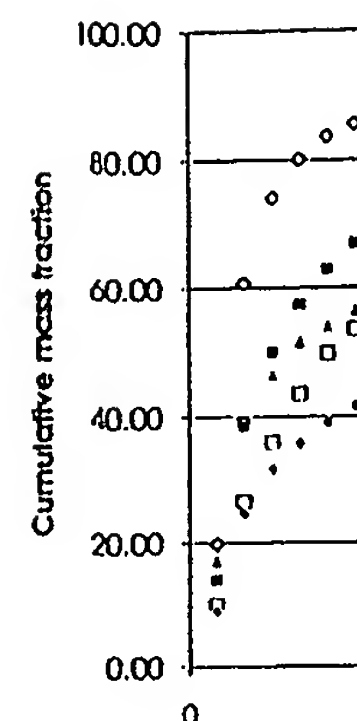


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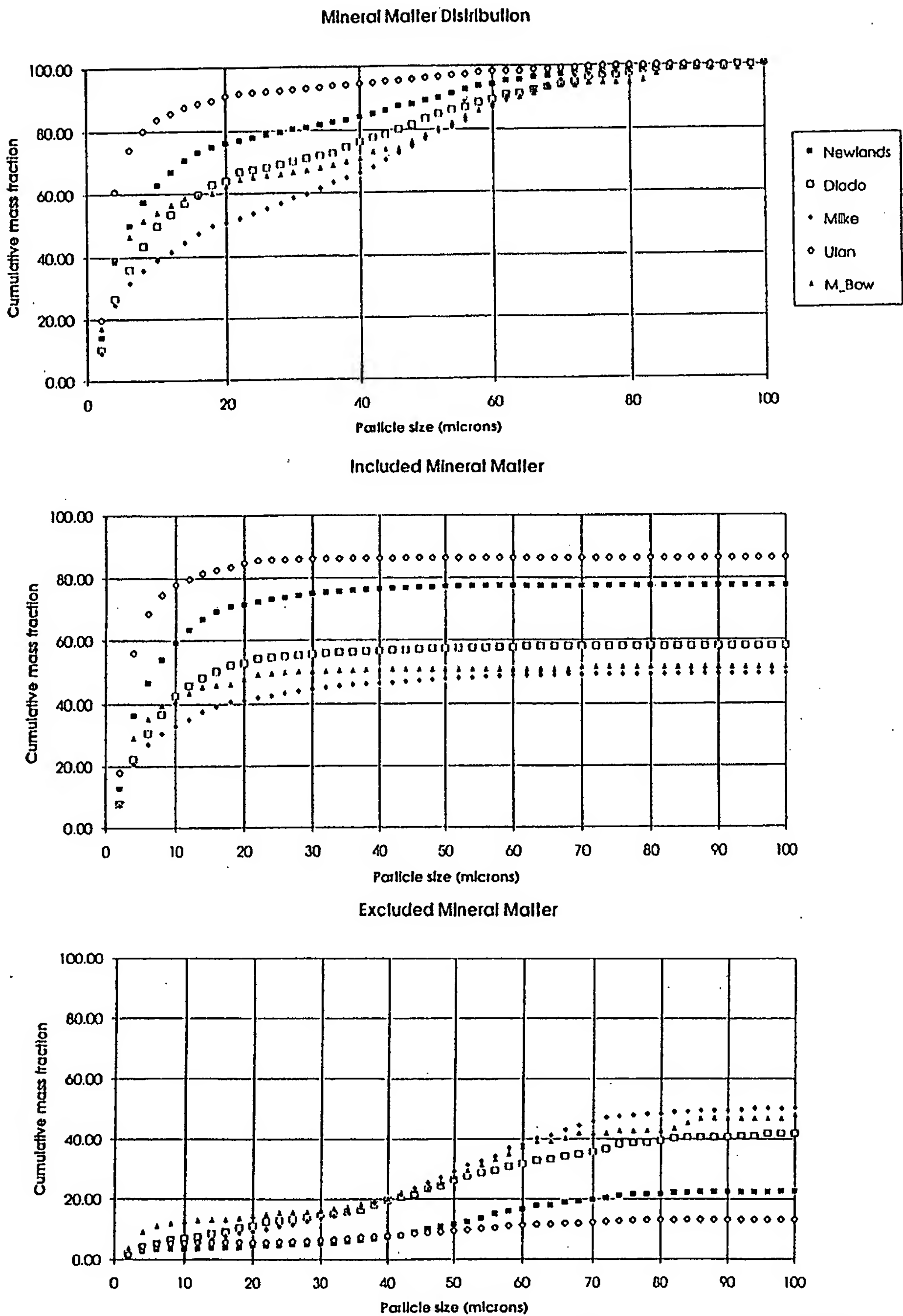


Figure 4. Particle size distribution of total, included and excluded mineral from CCSEM analysis.

of the mineral matter, detected by the CCSEM, shown in Figure 4a, is bimodal in nature due to different mean particle sizes for included and excluded minerals. Figures 4b and 4c show the PSD of the included and excluded mineral for the five coals. These figures suggest that most of the included mineral is in the range of 0-20 μ m, whereas the excluded mineral matter is mostly above 40 μ m in size. The particle size distribution of total, included and excluded silica, alumina, sodium oxide, calcium oxide and iron oxide is obtained similarly. The AC is evaluated for the included and excluded minerals independently.

The availability coefficient of excluded or included mineral is then computed from the particle size distribution by using the following correlation, where f_i is the mass fraction of excluded mineral in the size bin of radius r_i with t_i its reactive thickness.

$$AC = \frac{\sum f_i (1.0 - (r_i - t_i)^3 / r_i^3)}{\sum f_i} \quad (7)$$

The availability coefficient for a particular oxide depends on its reactive thickness. The reactive thickness for some synthetic ash particles formed at 1500°C was determined to be less than 1 μ m in laboratory experiments (Wibberley and Wall, 1980). The reaction layer thickness for the excluded minerals is assumed here to be 1 μ m. Since the included mineral matter determined from CCSEM encounters higher temperatures and extremely reducing environment within char, the thickness of the reaction layer for the fine grains of the included minerals is expected to be very high.

The amount of ash components obtained from the CCSEM analysis of minerals in coal is less than the ash determined from the XRF technique. This is mainly due to the fact that CCSEM cannot analyse sub-micron minerals and dissolved salts within the coal matrix. The amount and composition of this finer fraction has been estimated from the difference of those from XRF and CCSEM analyses. In the present calculations the AC for the included mineral together with the soluble salts and fine mineral matter, is assigned a value of unity.

3.2 Thermodynamic Equilibrium for Excluded Minerals

The excluded minerals are expected to be in thermal and chemical equilibrium with the flue gases. As the mineral reactions take place mostly within the flame, the composition of the surrounding flue gases is computed for a stoichiometric ratio of 0.8 (a reducing environment). The equilibrium calculations were performed at temperatures ranging from 1500°K to 3000°K.

Gas Phase: Predictions of the mole fraction of silica, iron, sodium and potassium in the gas phase are presented in Figure 5. The constant slope of $\log(x)$ vs $1/T$ in these figures suggests that the mole fraction of SiO and Fe species in the gas phase is directly proportional to the vapour pressure. At temperatures higher than 2500°K the complete evaporation of silica and iron from the excluded minerals is evident. Among the coals considered, Medicine Bow has the smallest mole fractions of all the ash components in the gas phase, while Miike has the highest mole fractions.

According to the experimental study by Srinivasachar et al. (1990), a higher concentration of alkalis would enhance the stickiness of the particles. The mole fractions of sodium and potassium in the gas phase increase with temperature. However, the mole fraction of these alkali components is not proportional to the vapour pressure of these components, but is controlled by the retention of these alkalis by silica in the molten phase. The mole fraction of sodium and potassium are also highest for Miike coal followed by Ulan, Daido and Newlands coals. Apart from Medicine-Bow coal, the mole fraction of alkalis appears to be one of the factors ranking the coals in the order of slagging.

Molten Phase: Figure 6 presents estimates of the molten phase per kg of ash content. This factor distributes the molten phase over the total ash. If the molten phase per unit of ash is low, it is expected to be less sticky, even if the total amount of molten phase is high. According to this criterion, Newlands and Ulan have the least amount of molten phase per unit of ash content and consequently have less sticky particles.

The calculations suggest that the quantity of the molten phase is not influenced significantly by the

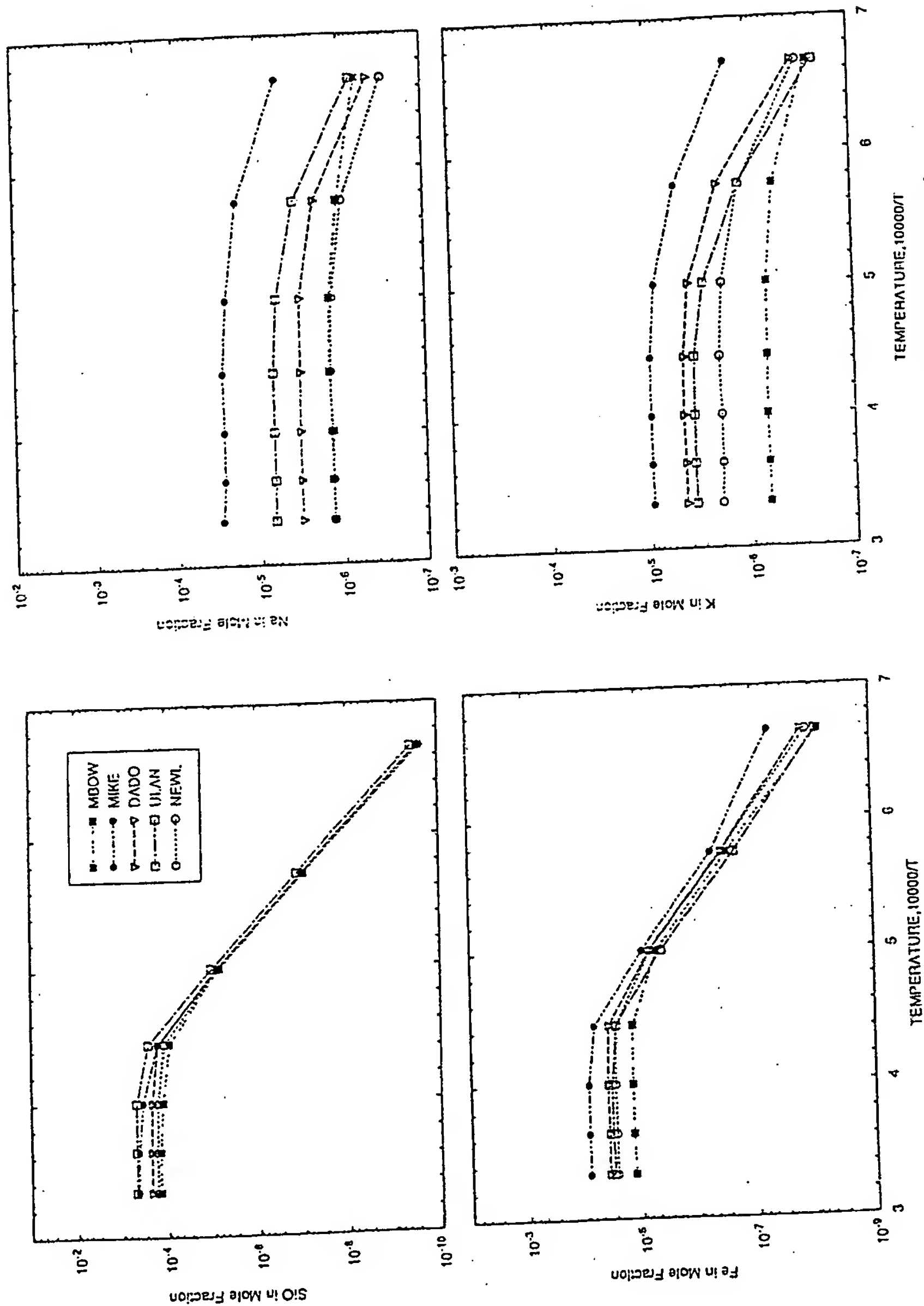


Figure 5. Mole fractions of SiO, Fe, Na and K in bulk gas phase predicted by thermodynamic calculations based on the excluded minerals in equilibrium with the flue gases.

combustion environment. However, the composition of the molten phase is affected. There is successive depletion of sodium, potassium and iron with an increase in the gas temperatures. The mole fractions of sodium, potassium and iron in the molten phase are minimum for Medicine-Bow and are maximum for Miike coal. The minimum values in the case of Medicine-Bow coal are due to high proportion of calcium and magnesium.

The mole fraction of calcium increases in the molten phase with an increase in temperature, which is due to a negligible evaporation of calcium oxide. At lower temperatures the molten phase has low melting point aluminosilicates of sodium and potassium, making the particles sticky. As the temperature rises, the concentration of calcium increases, giving rise to the sticky phase of calcium silicate. Therefore, in high calcium coals, the particles may be sticky even at higher temperature.

3.3 Thermodynamic Equilibrium for Included Minerals

The soluble salts and sub-micron size minerals (not detected by the CCSEM technique) and the included

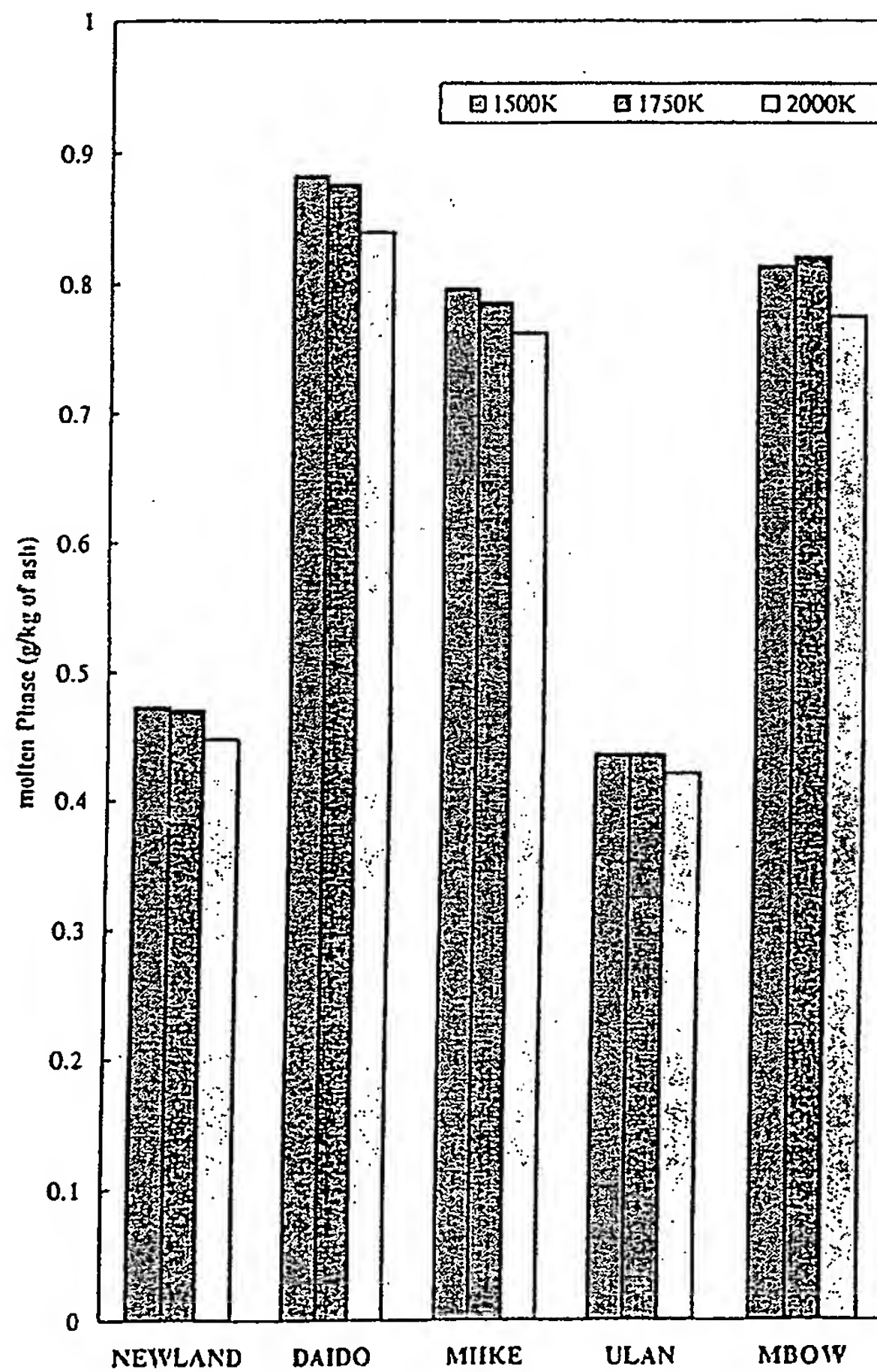


Figure 6. Theoretical amount of molten phase from excluded minerals per kg of ash.

minerals are in equilibrium with char and with the flue gases within the char particle. Thermodynamic calculations have shown that the mole fraction of SiO in the gas phase is at least two orders of magnitude higher in the presence of carbon. The availability coefficient of the mineral matter within the coal matrix is considered unity. The moles of gases in equilibrium with the included minerals are assumed to be equal to those present in 50% of the char volume at 2000°K.

The predicted mole fractions of silica, iron, calcium and magnesium correspond to the vapour pressure of these species in the presence of carbon. The mole fractions of these species increase exponentially until all is vaporised. A decrease in the amount of alkalis mole fraction with increase in particle temperature from 2000°K to 2500°K is due to relatively higher evaporation of silica, calcium and magnesium.

It is speculated that a part of these species diffuses from the char and condense to form fume. The rest of the species in the gas phase will cool and condense to form fine spherical particles. The concentration of the alkalis in the condensed phase is expected to be proportional to the initial concentration of the alkalis.

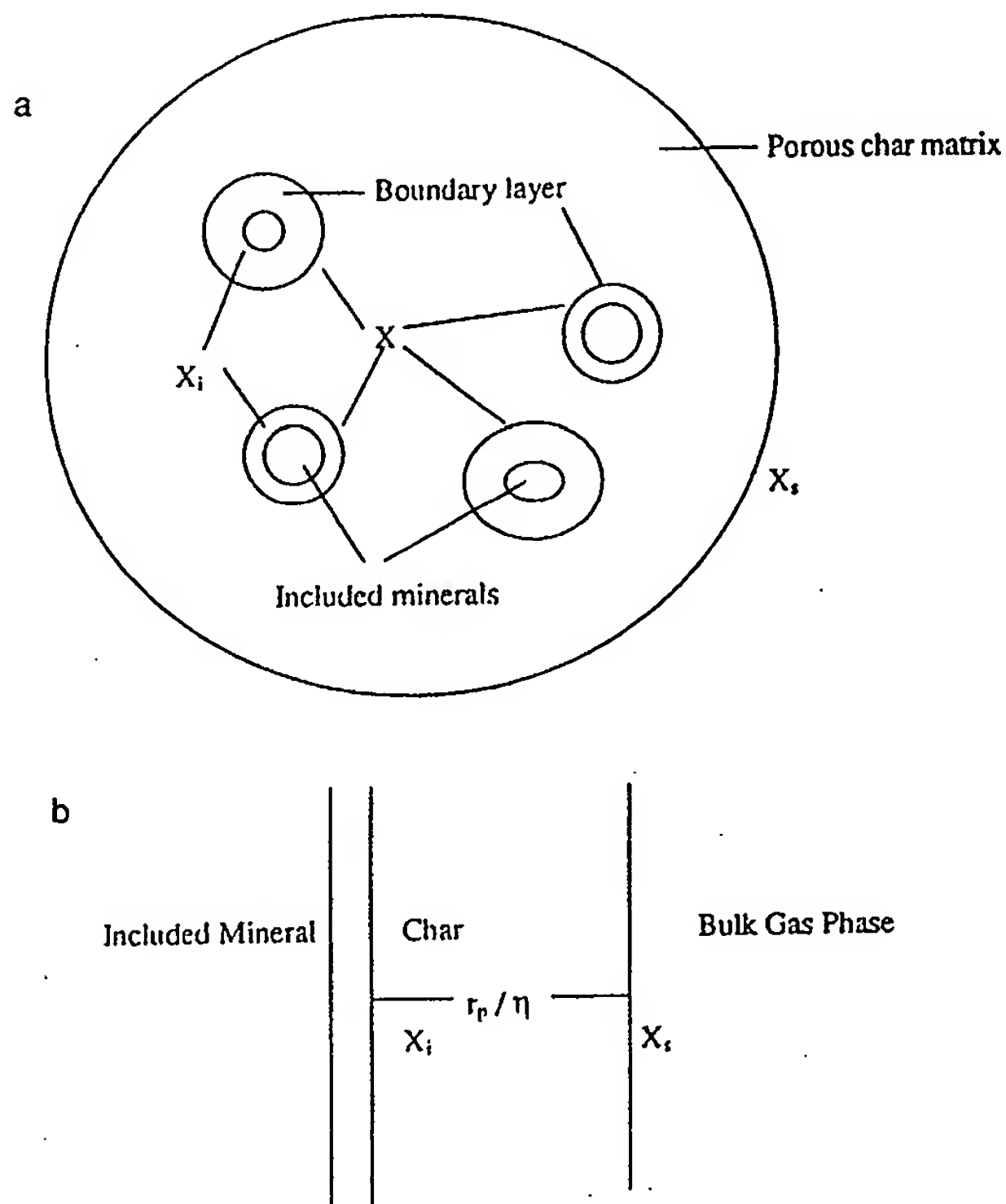


Figure 7. The schematic diagram for diffusion of mineral species from char to bulk gas phase (a) and the simplified model (b).

A high proportion of alkalis in Medicine-Bow and Miike coals results in low melting point silicates, and correspondingly, the included minerals will result in fine spherical ash particles (Figure 8). The size of these spheres observed in the ash from Medicine-Bow is small probably due to very low mineral loading of the coal particles. The ash formed from Ulan coal containing high proportions of silica will not have such low melting point compounds and hence it is expected to result in the formation of fluffy ash as shown in the Figure 8. These speculations on ash character are confirmed from the SEM images of the ash collected in the drop tube experiments.

The predicted mole fractions of the gaseous mixture within the burning char particles of Daido and Newlands coals are not very different. The mole fractions of sodium, potassium and magnesium for Newlands coal are higher than those from Ulan coal, whereas the mole fractions of iron and calcium are higher for Daido coal. A higher proportion of spherical particles present in the ash from Newlands coal is probably due to the formation of low melting point aluminosilicates of sodium and potassium having low melting temperatures.

4. DEVELOPMENT OF A DIFFUSION MODEL

The concentration of the mineral species in gas phase within burning char particles has been shown to be orders of magnitude higher than that in the bulk phase. The difference in the concentrations results in diffusion of these species into the bulk gas phase. These species will then form fine fumes as they oxidise and condense. At this stage it is expected that a major proportion of fumes would result from this process. The figure 7a shows a schematic diagram for the vaporising mineral inclusions in a char particle. The small hatched circles represent the mineral inclusions within the char particle. A boundary layer of the vaporising minerals is shown by concentric circles. A diffusion model for the transportation of vaporised minerals from the char into the surrounding gases is developed based on the following assumptions:

- The inclusions are of a single grain size and type, and are much smaller than the char particle. These are uniformly distributed in the char matrix.
- Vaporisation is limited by diffusion of mineral species from the surface of the mineral inclusions to the exterior surface of char.
- Vaporisation is driven by the gas phase concentration of the volatile species at the inclusion surface. This is modelled as diffusion from the inclusion surface to a mean concentration in the char, which is a function of the char particle radius.
- Diffusivity is constant through the pore matrix.
- The char combustion is assumed to be in pseudo-steady state in a stagnant gas of infinite extent.

The molar flux of the mineral species (J), determined by this model, is proportional to the driving force: the difference of the mole fractions at the inclusion (X_i) and at the char surface (X_s). The molar flux of the mineral species at the char surface ($r = r_p$) is given by the equation.

$$J = cD_{eff} 4\pi r_p (X_i - X_s) \eta \quad (8)$$

$$\text{where } \eta = \left[\frac{\Theta}{\tanh \Theta} - 1 \right] \text{ and } \Theta = \left(\frac{r_p}{r_i} \right) (3(\rho_p / \rho_i) \cdot f)^{0.5} \quad (9)$$

D_{eff} is the effective diffusivity of the mineral species in the char. The term η may be called an enhancement factor, by which the diffusion rate is enhanced. Θ can be considered as a modified Thiele modulus, a parameter characterising the dispersion of mineral matter within the char matrix. It is a function of mineral volume fraction f , the densities and radii of char particle and of mineral inclusions; a higher Thiele modulus inferring a better dispersion. All the complexities related to the mineral matter distribution within the char particle are lumped into a single enhancement factor given by equation (9).

In this simplified treatment the included minerals are on one side and the bulk gas phase on the other side of a char slab of thickness ($\Delta L = r_p / \eta$). A high enhancement factor reduces the path length implying a reduced diffusion resistance. Equation (8) is the equivalent of equation (10) for a simplified one dimensional system as shown in Figure 7b.

$$J = cD_{eff} (\text{Area} = 4\pi r_p^2) \cdot (\Delta X = \text{driving force}) / (\Delta L) \quad (10)$$

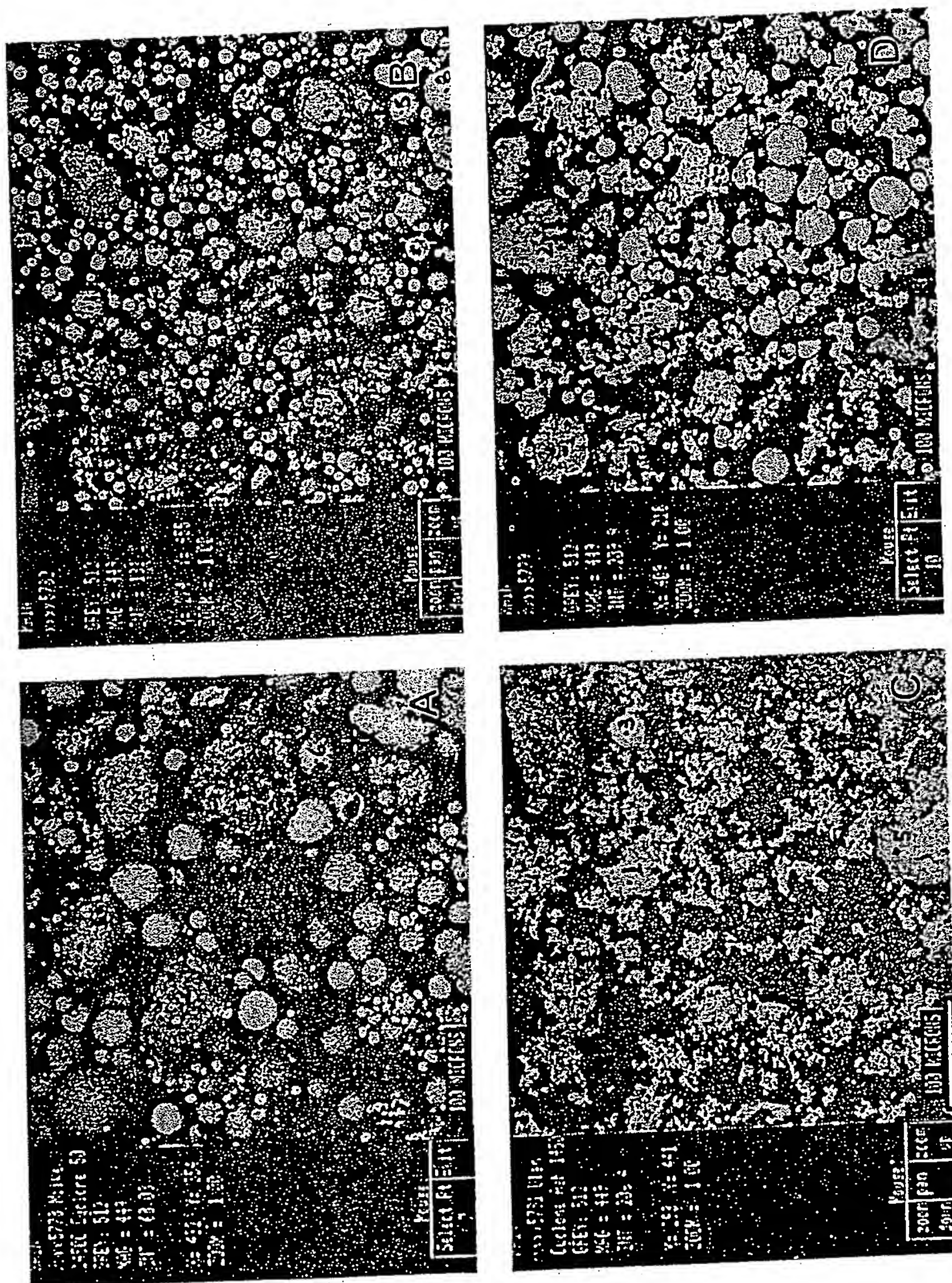


Figure 8. SEM images of ashes of Milke (A), Medicine-Bow (B), Newlands (C) and Ulan (D) coals prepared at 1450°C and in 50% oxygen environment.

Table 1: Ash analyses of the five coals.

Coals	Newlands	Daido	Miike	Ulan	Medicine Bow
Total Ash (%db)	11.95	7.58	17.5	22.0	4.7
SiO ₂	51.4	55.9	47.2	88.1	27.0
Al ₂ O ₃	32.0	24.9	20.0	7.9	10.4
TiO ₂	1.47	1.29	1.72	0.46	0.71
Fe ₂ O ₃	3.75	7.65	6.69	2.09	6.95
CaO	4.16	3.36	9.26	0.10	26.6
MgO	0.94	0.55	1.04	0.05	5.14
Na ₂ O	0.3	0.3	2.1	0.3	1.7
K ₂ O	0.79	1.08	0.76	0.3	0.28
P ₂ O ₅	1.95	0.6	0.23	0.03	0.13
SO ₃	3.18	4.23	10.9	0.64	21.26

Table 2. Ranking of coals in terms of ash deposition problems using the theoretical criteria defined in section 5.

Ash Deposition Ranking	Fumes/Fines (Bulk)	Gas Phase Alkalis (Bulk)	Molten Phase Comp (Ex Min)	Molten Phase Comp (In Min)
	Fouling Related	Slagging Related		
	Factor 1	Factor 2	Factor 3	Factor 4
High severity	Miike Ulan	Medicine-Bow Miike	Miike Daido Medicine-Bow	Miike Medicine-Bow
	Daido Newlands	Ulan	-	Daido Newlands
Low severity	Medicine-Bow	Newlands, Daido	Newlands Ulan	Ulan
Comments	Ranking agrees with that from the measured mass of fumes and fines from experiments.	-	-	Physical character observed in SEM images relates to theoretical melt composition

A higher ratio of the radii of char and mineral inclusions implies finely dispersed minerals in the char matrix. A high volume fraction of a finely dispersed phase of included minerals results in a high enhancement factor. For the same mineral loading the enhancement factor increases both with the particle size and the mineral loading. For diffusion of species, the surface area per g of coal, however, is inversely proportional to the radius of the char particles. A decrease in mineral size and increase in volume fraction of mineral matter enhance the diffusion of vapour species.

The molar flux of the mineral species is thus expressed as a function of $(X_i - X_s)$, the difference of mole fraction at the inclusion and char surface. The mole fraction of the species at the char particle surface is also a function of external transport. However, the diffusion of the species through the char particle may be considered as the controlling resistance. One can, therefore, determine the X_i from the equilibrium fraction of the included mineral matter within a char particle and X_s from the equilibrium fraction of the excluded mineral.

The concentration of the species at the char surface can be neglected compared to that at the inclusion surface. The rate of diffusion of these species will, therefore, be determined primarily from the mole fractions within burning char particle resulting from the included minerals. An estimation of the total diffusion of species requires the integration of equation (8) over the burning time of the char particle. The burning time and the particle temperature for 50% oxygen environment do not differ significantly with coal type. Assuming X_i and D_{eff} does not vary during combustion time, the amount of fumes diffusing out of particles is directly proportional to η , the enhancement factor.

The enhancement factor depends on the mineral loading and the ratio of particle size to that of the mineral grain. The total mineral volume fraction in the char particle varies from about 2% for Medicine-Bow coal to about 10% for Ulan coal (based on minerals having twice the density of char). From the CCSEM data, the ratios of particle radius to mineral inclusion radius are taken to be 50 for the fines and dissolved salts and 4 for the other included minerals.

The mole fraction of total inorganics in the gas phase is found to be similar for different coals. This implies that the diffusion rate of total mineral species increases with an increase in the enhancement factor. The enhancement factor thus obtained is 1.2, 1.8 2.6 4.0 and 4.5 for Newlands, Daido, Miike, Ulan and Medicine-Bow coals respectively. The rate of fumes generated is greatest for the Medicine-Bow coal, followed by Ulan coal. Accordingly, the coals are ranked in the following order: Newlands as the least fouling prone coal, Daido, Miike, Ulan and Medicine-Bow coal as the most fouling prone coal. The high levels of alkalis will make the fumes from Medicine-Bow very sticky. The high mole fraction of silica and low levels of alkalis in the fumes from Ulan coal will result in dry ash. This ranking considers the contribution of fumes from the excluded minerals is comparatively negligible.

4.1 Comparison of fumes generated

The ash collected in the drop tube furnace experiments was analysed both for fines and coarse ash compositions. The fine ash rich in fumes, collected on a filter paper, is mostly finer than $2\mu\text{m}$ in size and results from the diffusion of evaporated mineral species from char and also from fragmentation. The remaining ash collected as coarse ash is mostly greater than $2\mu\text{m}$ in size. The amount of fines, thus collected, were negligible for Newlands and Daido coals. The fines generated for the Medicine-Bow coal (1g/100g of coal) were a magnitude higher than those for Ulan and Miike coals (0.1-0.12 g/100g of coal) at 1450°C and 50% oxygen.

D_{eff} can vary from $0.05\text{ cm}^2/\text{s}$ to $5.0\text{ cm}^2/\text{s}$ for Knudsen diffusion and bulk diffusion limits, respectively. The amount of fumes diffused from 100g of coal, for a D_{eff} of $0.05\text{ cm}^2/\text{s}$, from the char particles in 0.1s (typical burnout time for $80\mu\text{m}$ particle in 50% oxygen concentration) is of the order of 0.06g for Miike coal and 0.12g for Medicine-Bow coals, respectively. A high porosity of low rank coals (eg char from Medicine-Bow coal) would probably result in a higher D_{eff} indicating a better match with the experimental value. The experimental values for fines are higher probably due to fines generated by fragmentation of char.

The fumes generated in 1250°C and 50% oxygen environment were estimated to be of similar magnitude

from the experiments. Theoretically, there is no significant difference in the temperatures of the burning char particles under the two experimental conditions. The theoretical estimates for the fumes and fines generated would, therefore, be same under the two environments.

4.2 Character of ash particles from Included Minerals

The included minerals transformed at high temperature in a reducing environment are expected to result in spherical particles. The proportion of spherical particles and their size, inferred from the thermodynamic equilibrium composition, may be compared with the SEM images of the ashes collected from the drop tube furnace experiments in Figure 8. This is based on the assumption that a larger proportion (by number) of ash particles are derived from the included minerals.

It has been demonstrated from the thermodynamic calculations that at particle temperatures higher than 2500°K, (corresponding to 50% oxygen and 1450°C environment) all the included minerals species except for alumina vaporise. At present it is speculated that a fraction of these species will diffuse from the char and condense to form fume. The rest of the species will cool and condense to form spherical particles - small from the coals with low mineral content and large from the coals with high mineral content. The particles will be perfect spheres for coals having high alkali contents, but may be non-spherical fluffy particles for included minerals of coals low in alkali content.

A high proportion of alkalis in Medicine-Bow and Miike coals would, therefore, result in low melting point silicates and, subsequently, the included minerals will transform into fine spherical ash particles. The size of these spheres observed in the ash from Medicine-Bow coal is rather small probably due to very small mineral loading of the coal particles. The ash formed from Ulan coal containing high proportions of silica should have compounds of high melting point and hence is expected to result in the formation of fluffy ash. The SEM images of the ash collected in the drop tube experiments agree with the predictions. A higher proportion of spherical particles observed in the ash from Newlands is probably due to the formation of low melting point aluminosilicates of sodium and potassium.

The presence of spherical ash particles as those derived from Medicine-Bow and Miike coals indicates sticky particles, whereas, the fluffy ash particles from Ulan coal are not expected to be sticky. Accordingly, Medicine-Bow and Miike coals are ranked as the most difficult regarding ash deposition, Newlands and Daido coals as moderate, and Ulan coal having the least problems in terms of ash deposition.

5. IMPLICATIONS FOR FOULING AND SLAGGING

There are a number of criteria that need to be considered when developing indices for ranking coals for stickiness and subsequently slagging and fouling tendencies. Table 2 gives the ranking of the five coals with respect to each of these criteria.

1. The amount of fumes and fines: The contribution to the fines from the excluded mineral is greatest from Miike and Ulan coals and is minimum for the Medicine-Bow coal. However, the contribution from the included minerals is greatest from the Medicine-Bow coal, followed and Miike, Ulan and is the least for Newlands coal as seen from their respective enhancement factor. Simple calculations show that the contribution from included mineral is the dominant factor and thus ranks the coal in fouling tendencies.

2. The concentration of alkalis in bulk gas phase: The presence of alkalis in the bulk gas phase is expected to cause sticky ash particles. The concentration of alkalis due to excluded minerals would rank the coals in the order of Miike, followed by Ulan, Daido, Newlands and Medicine-Bow coals. The contribution from the included mineral is greatest for Medicine-Bow and Miike coals and would dominate the alkalis in the gas phase.

3. The molten phase associated with excluded minerals: The amount of molten phase on the excluded minerals per unit of total ash is related to the proportion of binding component on the ash particles and this criterion ranks Miike, Medicine-Bow and Daido coals as severely slagging coals compared to Newlands and Ulan coals.

4. The gas phase from spherical particles present

Confirmation of mineral species from the Miike by the SEM images

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4. The molten phase associated with included minerals: The theoretical estimates of the composition in the gas phase inside the burning char particle, indicate the formation of fine spherical ash particles resulting from combustion of Medicine-Bow coal. The ash particles from Miike coal are also predicted to be spherical but large, and to be comparatively sticky in nature. Ulan coal, due to its composition of gas phase present within the char particle, is expected to be fluffy and non-sticky.

Confirmation with Experiments: The fumes and fines are expected to result mostly from the included minerals and the theoretical ranking of coals based on this criterion agrees with trends from the experiments. The theoretical amount of fumes and the amount of fine ash from experiments from the Miike coal is of similar magnitude. Also the speculations on the physical character of ash, suggested by the theoretical composition of the molten phase generated by the inherent minerals, agree with the SEM images of the ash collected in the experiments.

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STUDIES

ABSTRACT

The release of aluminium, iron, and other trace elements from #8 coal, peat, and wood under various conditions is studied. The results show that during the pyrolysis of these fuels, various elements are released from the solid phase into the gas phase.

INTRODUCTION

The behavior of trace elements in fuels during combustion and ash deposition is of interest to the power industry. The formation of corrosion products from bound inorganic minerals as ash is mainly determined by the Kirkby, 1970 conversion process. The oxidation of

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